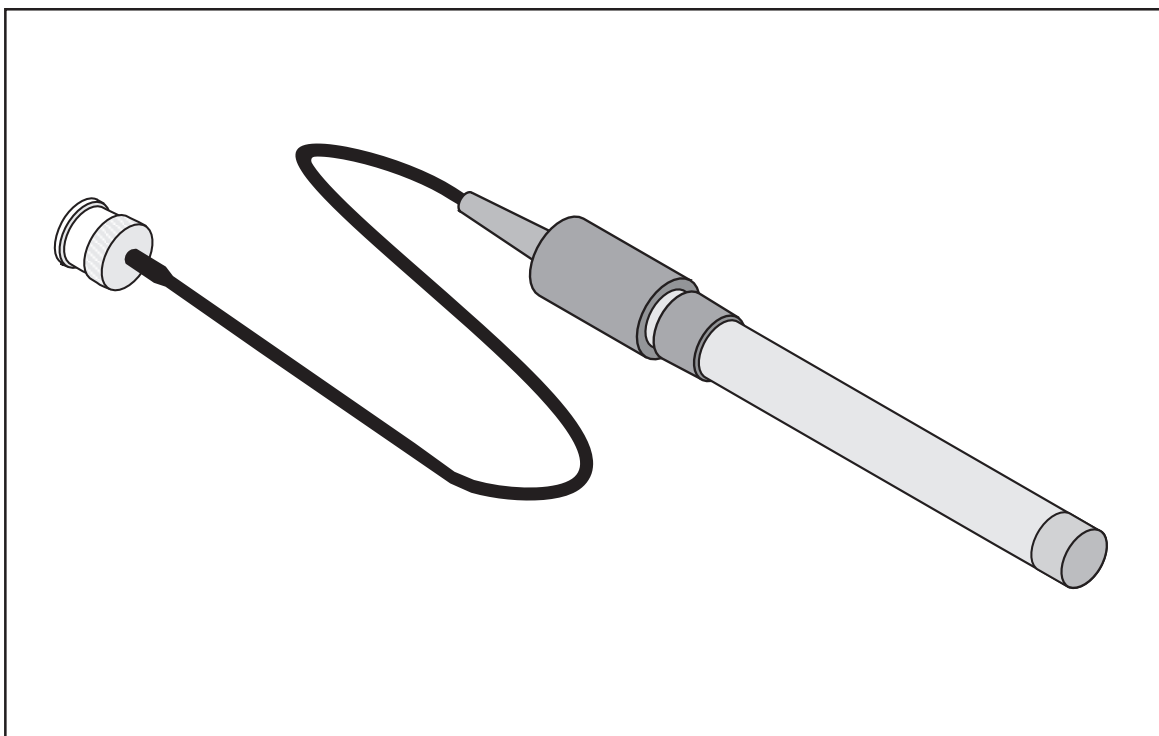


***Instruction Manual and  
Experiment Guide for the  
PASCO scientific  
Model CI-6727***

012-06601A

9/97

# ***CALCIUM SELECTIVE ELECTRODE***



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\$7.50



**Always use eye protection  
and gloves when working  
with chemicals.**

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## Introduction

The PASCO Calcium Ion Selective Electrode is used to quickly, simply, accurately, and economically measure calcium concentration in aqueous solutions.

## Theory

The Calcium Ion Selective Electrode consists of an electrode body containing an ion exchanger in a sensing module. This sensing module contains a liquid internal filling solution in contact with a gelled organophilic membrane containing a calcium ion selective exchanger.

An electrode potential develops across the membrane. When the membrane is in contact with a calcium solution. Measurement of this potential against a constant reference potential, using an ISE Amplifier and Science Workshop interface, depends on the level of free calcium ion in solution. The level of calcium ions, corresponding to the measured potential, is described by the Nernst equation:

$$E = E_0 + S \log X$$

where:

$E$  = measured electrode potential

$E_0$  = reference potential (a constant)

$S$  = electrode slope (~26 mv/decade)

$X$  = level of calcium ions in solution

The activity,  $X$ , represents the effective concentration of the calcium ions in the solution. Total calcium concentration,  $C_t$  includes free calcium ions,  $C_f$  plus bound or complexed calcium ions,  $C_b$ , since the calcium electrodes only respond to free ion, the free ion concentration is:

$$C_f = C_t - C_b$$

The activity is related to the free ion concentration,  $C_f$ , by the activity coefficient,  $\gamma$ , by:

$$X = \gamma C_f$$

Activity coefficients vary, depending on total ionic strength,  $I$ , defined as:

$$I = 1/2 \sum C_x Z_x^2$$

where:

$C_x$  = concentration of ion  $X$

$Z_x$  = charge on ion  $X$

$\Sigma$  = sum of all of the types of ions in the solution

In the case of high and constant ionic strength, relative to the sensed ion concentration, the activity coefficient,  $\gamma$ , is constant and the activity,  $X$ , is directly proportional to the concentration.

To adjust the background ionic strength to a high and constant value, ionic strength adjuster (ISA) is added to samples and standards. The recommended ISA solution for calcium is potassium chloride, KCl. Solutions other than this may be used as ionic strength adjusters as long as ions that they contain do not interfere with the electrode's response to calcium ions.

The reference electrode must also be considered. When two solutions of different composition are brought into contact with one another, liquid junction potentials arise. Millivolt potentials occur from the inter-diffusion of ions into the two solutions. Electrode charge will be carried unequally across the solution boundary resulting in a potential difference between the two solutions, since ions diffuse at different rates. When making measurements, it is important to remember that this potential be the same when the reference is in the standardizing solution as well as in the sample solution or the change in liquid junction potential will appear as an error in the measured electrode potential.

The composition of the liquid junction, filling solution in the reference electrode is most important. The speed with which the positive and negative ions in the filling solution diffuse into the sample should be equitransferent. No junction potential can result if the rate at which positive and negative charge carried into the sample is equal.

## Equipment

### Included:

- Calcium Ion Selective Electrode
- Calcium Ion Selective Electrode fill solution
- pipette for fill solution

### Additional Required:

#### Required Equipment

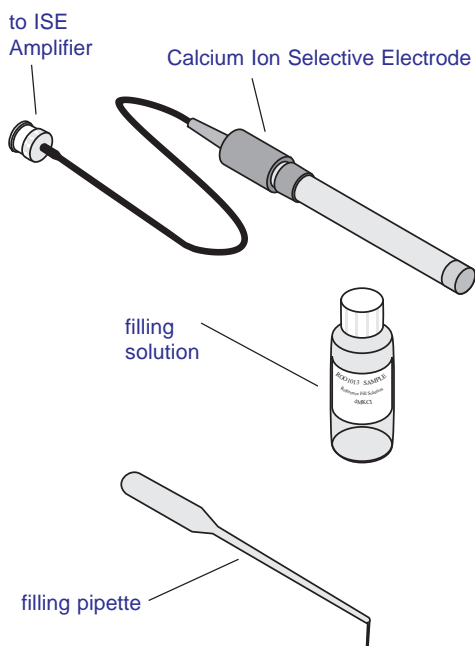
- PASCO CI-6738 ISE (Ion Selective Electrode) Amplifier
- *Science Workshop 2.25* or higher

- PASCO *Science Workshop* Computer Interface
- Semi-logarithmic 4-cycle graph paper for preparing calibration curves (Linear graph paper is recommended for low level measurements)
- magnetic stir plate
- Lab-ware made of plastic, not glass, for all low level measurements.

## Required Solutions

The stock solutions listed in this section may be created as described in the text or ordered directly from PASCO. The solutions available for order and their respective prices are listed on the 'ISE Working Solution Price List'.

- Deionized or distilled water for solution and standard preparation.
- *Calcium Chloride solution 0.1M  $\text{CaCl}_2$*   
To prepare this solution, half fill a one liter volumetric flask with distilled water and add 14.7 grams of reagent-grade calcium chloride ( $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ ). Swirl the flask gently to dissolve the solid. Fill to the mark with distilled water, cap, and upend several times to mix the solution.
- *Calcium Chloride solution 1000 ppm  $\text{Ca}^{+2}$*   
To prepare this solution, half fill a one liter volumetric flask with distilled water and add 3.67 grams of reagent-grade calcium chloride ( $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ ). Swirl the flask gently to dissolve the solid. Fill to the mark with distilled water, cap, and upend several times to mix the solution.
- *Calcium Chloride solution 100 ppm  $\text{Ca}^{+2}$  as  $\text{CaCO}_3$*   
To prepare this solution, half fill a one liter volumetric flask with distilled water and add 0.15 grams of reagent-grade calcium chloride ( $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ ). Swirl the flask gently to dissolve the solid. Fill to the mark with distilled water, cap, and upend several times to mix the solution.



**Figure 1**  
Included Equipment

- *Ionic Strength Adjuster (ISE), 4 M KCL*

To prepare this solution, half fill a 1000 ml volumetric flask with distilled water and add 298 grams of reagent-grade potassium chloride (KCl). Swirl the flask gently to dissolve the solid. Fill to the mark with distilled water, cap, and upend several times to mix the solution.

- *EDTA titrant, 1 M stock solution, for the titration of calcium*

To prepare this titrant, add 37.2 grams of reagent grade  $\text{Na}_2\text{EDTA} \cdot 2\text{H}_2\text{O}$ , ethylenediaminetetraacetic acid dihydrate, disodium salt, to a 100 ml volumetric flask, add about 75 ml of distilled water, and swirl the flask gently to dissolve the solid. Fill to the mark with distilled water, cap, and upend several times to mix the solution.

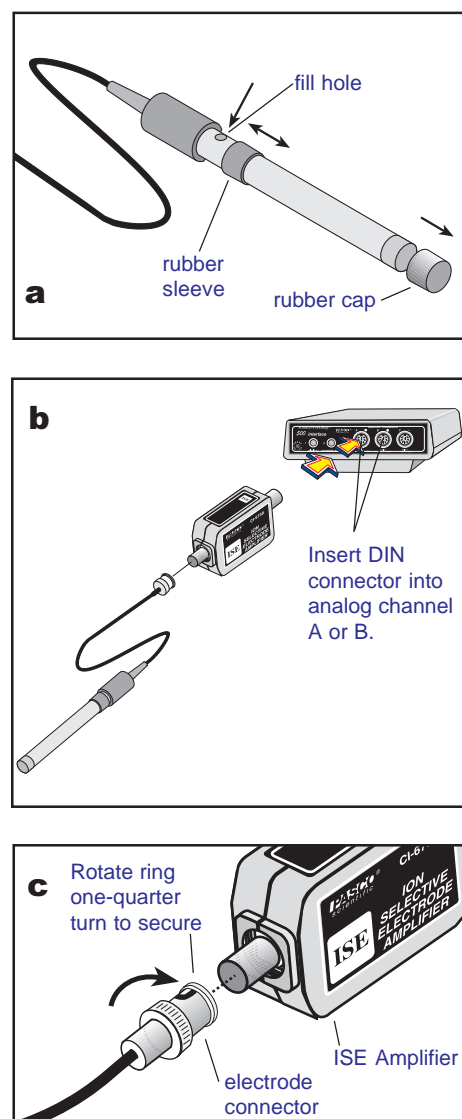
## General Preparation

### Electrode Preparation

1. Remove the rubber cap covering the electrode tip. Slide the rubber sleeve down away from the filling hole of the Calcium Selective Ion Electrode. Fill the electrode with the included filling solution to a level just below the fill hole. Slide the rubber sleeve back over the filling hole (Figure 2a).
2. Gently shake the electrode downward in the same manner as a clinical thermometer to remove any air bubbles which might be trapped behind the calcium membrane. Prior to first usage, or after long-term storage, immerse the calcium membrane in calcium standard for thirty minutes.
3. Connect the Calcium Selective Ion Electrode to the ISE Amplifier and insert the DIN connector of the ISE Amplifier into analog channel A or B on a PASCO Computer Interface (Figures 2b and 2c).

### Electrode Slope Check Using *ScienceWorkshop* (check electrodes each day)

1. To a 150 ml beaker, add 100 ml of distilled water. Place the beaker on a magnetic stirrer and begin stirring at a constant rate. Start Science Workshop, select the Ion Selective Electrode sensor, open a Digital display, and begin monitoring data. Lower the electrode tip into the solution.
2. Using a pipette, add 1 ml of 0.1 M, 1000 ppm, or 100 ppm (as calcium carbonate) standard and 2 ml of ISA to the beaker. When the reading has stabilized, record the voltage reading indicated in the Digits display.



**Figure 2**  
Equipment Setup. **a:** filling the electrode with filling solution; **b & c:** connecting the electrode to the ISE Amplifier and to the computer interface

3. Using a pipette, add 10 ml of the same calcium standard used above to the beaker. When the reading has stabilized, record the voltage reading indicated in the Digits display.
4. Determine the difference between the two readings. The electrode is operating correctly if the potential has changed by  $26 \pm 2$  mV, assuming the temperature is between 20°C and 25°C. See the **Troubleshooting** sections if the potential change is not within this range.

► **Note:** *Slope is defined as the change in potential observed when the concentration changes by a factor of 10.*

## Measurement

### Measuring Hints

- All samples and standards should be at the same temperature for precise measurement. A difference of 1 °C in temperature will result in a 4% measurement error.
- The sensing membrane is normally subject to water uptake and might appear milky. This has no effect on performance.
- Constant, but not violent stirring is necessary for accurate measurement. Magnetic stirrers can generate sufficient heat to change the solution temperature. To counteract this effect, place a piece of insulation material, such as a styrofoam sheet, between the stirrer and beaker.
- Always rinse the electrodes with distilled water and blot dry between measurements. Use a clean, dry tissue to prevent cross-contamination.
- For samples with high ionic strength, prepare standards whose composition is similar to the sample.
- Always check to see that the membrane is free from air bubbles after immersion into the standard or sample.
- A slow responding electrode may be caused by interferences to the electrode. To restore proper performance, soak the electrode in distilled water for about 5 minutes to clean the membrane, rinse, and soak in diluted standard solution for about 5 minutes.
- Dilute concentrated samples (over 0.1M) before measurement.
- Recalibrate every few hours for routine measurement.

### Sample Requirements

- All samples must be aqueous and not contain organics which can dissolve the membrane or extract out the liquid ion exchanger.
- The temperature of the standard solutions and of the sample solutions should be the same and below 40°C. About a 2% error in the slope will occur for each 1°C difference in temperature.
- The pH range for the calcium ion electrode is 3-10. Neutralize samples outside this range with NaOH or HCl to bring them in range.
- Interferences should be absent. If they are present, use the procedure found in the **Interferences** and **Electrode Response** sections to remove them.

### Units of Measurement

Calcium concentrations are measured in units of ppm as calcium, ppm as  $\text{CaCO}_3$ , moles per liter, or any other convenient concentration unit. Table 1 indicates some concentration units and conversion factors.



**TABLE 1      Concentration Unit Conversion Factors**

<i>ppm Ca<sup>+2</sup></i>	<i>ppm CaCO<sub>3</sub></i>	<i>moles/liter</i>
4.01	10.0	1.0 X 10 <sup>-4</sup>
10.00	24.9	2.5 X 10 <sup>-4</sup>
40.10	100.1	1.0X10 <sup>-3</sup>
400.80	1000.9	1.0 X 10 <sup>-2</sup>

## Measurement Procedure

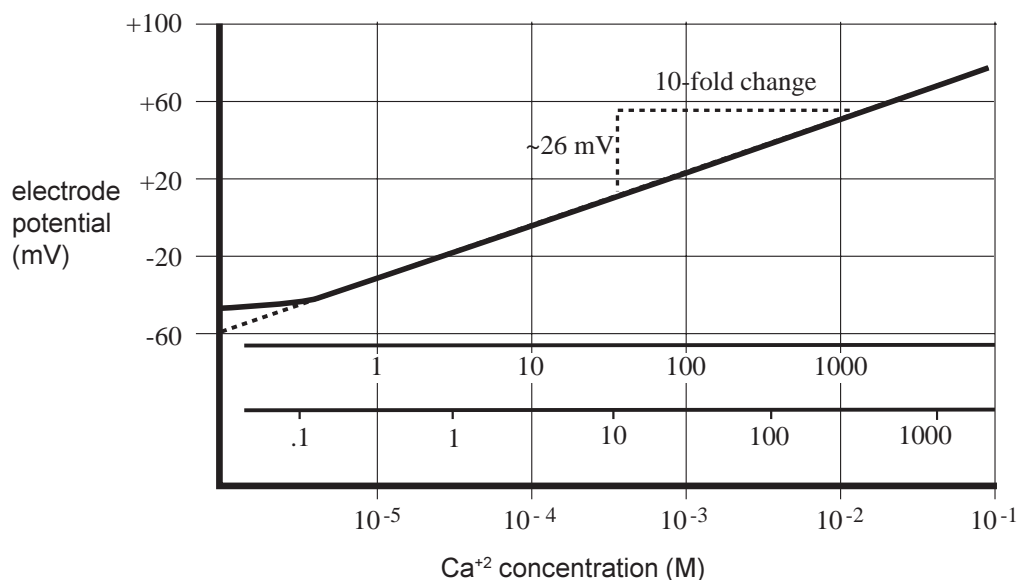
### Direct Measurement

Direct measurement is a simple procedure for measuring a large number of samples. A single meter reading is all that is required for each sample. The ionic strength of samples and standards should be made approximately the same by adjustment with ISA. The temperature of both sample solution and standard solution should be the same.

#### Direct Measurement of Calcium

**► Note:** *A calibration curve is constructed on semi-logarithmic paper. The measured electrode potential (linear axis) is plotted against the standard concentration (log axis). In the linear region of the curve, only two standards are necessary to determine a calibration curve. Calibration standards close to the anticipated value of the “unknown” should be chosen. In the non-linear region, additional points must be measured. The direct measurement procedures given are for the linear portion of the curve. The non-linear portion of the curve requires the use of low level procedures.*

1. By serial dilution, prepare three standard solutions from the 0.1M, 100 ppm, or 100 ppm standard. The resultant concentrations should be 10<sup>-2</sup> M, 10<sup>-3</sup> M, and 10<sup>-4</sup> M or 100, 10 and 1 ppm standards. Add 2 ml of ISA to each 100 ml of standard.
2. Place the most dilute solution (1.0 X 10<sup>-4</sup> M or 1 ppm) in a 150 ml beaker on the magnetic stirrer and begin stirring at a constant rate. After assuring that *Science Workshop* is operating, lower the electrode tip into the solution. When the reading has stabilized, record the voltage reading indicated in the Digits display.
3. Place the mid-range solution (1.0 X 10<sup>-3</sup> M or 10 ppm) in a 150 ml beaker on the magnetic stirrer and begin stirring. Add 2 ml of ISA. After rinsing the electrodes with distilled water, blot dry, and immerse the electrode tips in the solution. When the reading has stabilized, record the voltage reading indicated in the Digits display.
4. Place the most concentrated solution (1.0 X 10<sup>-2</sup> M or 100 ppm) in a 150 ml beaker on the magnetic stirrer and begin stirring. After rinsing the electrodes with distilled water, blot dry, and immerse the electrode tip in the solution. When the reading has stabilized, record the voltage reading indicated in the Digits display.
5. Using the semi-logarithmic graph paper, plot the voltage reading (linear axis) against the concentration (log axis). Extrapolate the calibration curve down to about 2.0 X 10<sup>-6</sup> M. A typical calibration curve can be found in Figure 3.



**Figure 3**  
Typical calcium electrode calibration curve

- To a clean, dry, 150 ml beaker, add 100 ml of the sample, 2 ml of ISA, and 2 ml of ISA. Place the beaker on the magnetic stirrer and begin stirring at a constant rate. Rinse the electrode with distilled water, blot dry, and lower the electrode tip into the solution. When the reading has stabilized, record the voltage reading indicated in the Digits display. Using the calibration curve, determine the sample concentration.
- The calibration should be checked every two hours. Assuming no change in ambient temperature, immerse the electrode tip in the mid-range standard. After the reading has stabilized, compare it to the original reading recorded in step 3 above. A reading differing by more than 0.5 mV or a change in the ambient temperature will necessitate the repetition of steps 2–5 above. A new calibration curve should be prepared daily.

## Low Level Calcium Determination

This procedure is recommended for solutions with ionic strengths less than  $1.0 \times 10^{-2}$  M. If the solution is high in ionic strength, but low in calcium, use the same procedure, but prepare a calibration solution with a composition similar to the sample.

- Dilute 10 ml of the 0.1M standard to 1000 ml to prepare a  $1.0 \times 10^{-3}$  M standard solution for measurements in moles per liter. Dilute 10 ml of the 1000 ppm or 1 ml of the 100 ppm standard to 1000 ml to prepare a 10 ppm standard solution for measurements in ppm.
- Soak the calcium electrode for at least 1 hour in  $1.0 \times 10^{-3}$  or 100 ppm calcium standard solution.
- To a 150 ml beaker, add 100 ml of distilled water. Place the beaker on the magnetic stirrer and begin stirring at a constant rate.
- Place the electrode tips in the solution. Assure that the meter is in the mV mode.

5. Add increments of the  $1.0 \times 10^{-3}$  M or 10 ppm standard as given in Table 2 below.
6. After the reading has stabilized, record the voltage reading indicated in the Digits display after each addition.

**TABLE 2: Step-wise Calibration For Low Level Calcium Measurements**

Step	Pipette	Added Volume (ml)	<u>Concentration</u>	
			M	ppm
1	A	0.1	$1.0 \times 10^{-6}$	$1.0 \times 10^{-2}$
2	A	0.1	$2.0 \times 10^{-6}$	$2.0 \times 10^{-2}$
3	A	0.2	$4.0 \times 10^{-6}$	$4.0 \times 10^{-2}$
4	A	0.2	$6.0 \times 10^{-6}$	$6.0 \times 10^{-2}$
5	A	0.4	$9.9 \times 10^{-6}$	$1.0 \times 10^{-1}$
6	B	2.0	$2.9 \times 10^{-5}$	$2.9 \times 10^{-1}$
7	B	2.0	$4.8 \times 10^{-5}$	$4.8 \times 10^{-1}$

Pipet A = 1 ml graduated pipette

Pipet B = 2 ml pipette

Solutions: additions of 10 ppm or  $1.0 \times 10^{-3}$  M standard to 100 ml of distilled water.

7. On semi-logarithmic graph paper, plot the mV reading (linear axis) against the concentration (log axis) as in Figure 1.
8. Rinse the electrodes in distilled water and blot dry.
9. Measure out 100 ml of the sample into a 150 ml beaker and place the beaker on the magnetic stirrer and begin stirring. Lower the electrode tips into the solution. After the reading has stabilized, record the mV reading and determine the concentration from the low level calibration curve.
10. Prepare a new low level calibration curve daily. Check the calibration curve every 1-2 hours by repeating Steps 2-7 above.

## Titration

The progressive and quantitative addition of a reagent to a measured sample until neither active species (reagent or sample) is in excess. Ion selective electrodes are excellent endpoint detectors since they are not influenced by solution color or turbidity. Though titration is more time consuming than direct measurement, it is about 10 times more accurate.

### Titration of Calcium

The method outlined in this section makes use of the calcium ion electrode as a highly sensitive endpoint detector for calcium-containing samples. The titrant used is EDTA.

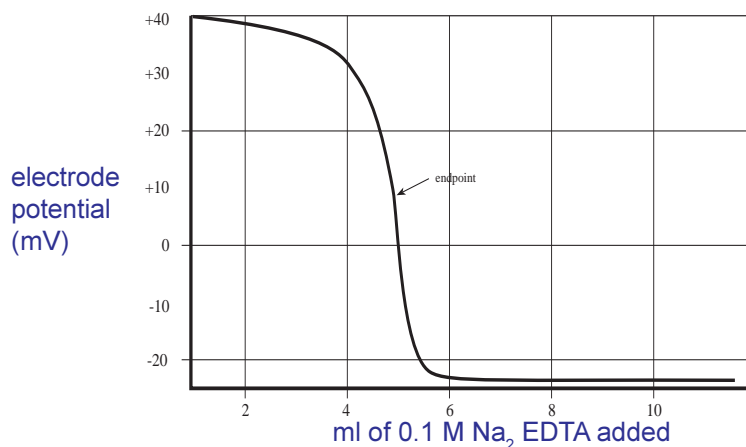
EDTA complexes calcium as well as other cations. The sample pH can be adjusted to pH 10 by adding ammonia to eliminate unwanted ion complexes. Masking agents can be added in some cases.

1. Soak the calcium ion electrode tip in  $10^{-3}$  M or 100 ppm calcium standard solution for a minimum of one hour prior to use.

2. Prepare the stock EDTA titrant as given in the section Required Solution. Dilute the EDTA to 10 to 20 times as concentrated as the suspected sample concentration. The sample should contain at least  $1.0 \times 10^{-3} \text{ M}$  calcium for a good detection of the endpoint.
3. Fill a 50 ml buret with the EDTA solution. Pipette 100 ml of the sample into a 150 ml beaker, place the beaker on the magnetic stirrer and begin stirring at a constant rate. Adjust the sample to pH 10 by adding ammonia.
4. Position the buret tip in the beaker, slightly above the liquid level in the beaker and slightly off center. Position the electrode tips in the solution about half way between the center of the beaker and the beaker wall.
5. Begin adding the EDTA in 0.5 ml to 1.0 ml increments and about 0.1 ml to 0.2 ml increments as the potential begins to change more rapidly. Record the mV potential after each addition. Continue the additions several milliliters past the endpoint.
6. Plot the milliliters of EDTA added against the mV potential on standard coordinate graph paper (See Figure 4). The point of greatest potential change is the endpoint .

**Figure 4**

Typical titration of 100 ml of  $5 \times 10^{-3} \text{ M}$  CaCl<sub>2</sub> (ph adjusted to ~10 with ammonia with 0.1 M Na<sub>2</sub> EDTA



7. The calcium ion concentration from the unknown is calculated as follows:

$$M_{Ca^{+2}} = \frac{V_t M_t}{V_{Ca^{+2}}}$$

where:

$M_{Ca^{+2}}$  = concentration of calcium ion in the unknown (moles/liter)

$V_t$  = volume of EDTA added at endpoint

$M_t$  = EDTA concentration (moles/liter)

$V_{Ca^{+2}}$  = volume of unknown sample

## Electrode Characteristics

### Reproducibility

Electrode measurements reproducible to  $\pm 4\%$  can be obtained if the electrode is calibrated every hour. Factors such as temperature fluctuations, drift, and noise limit reproducibility. Reproducibility is independent of concentration within the electrode's operating range.

### Interferences

Table 3 lists some common cautions that, if present in high enough levels, will cause electrode interferences and measurement errors or electrode drift when using the calcium electrodes.

Electrode drift and slow response could indicate the presence of high interferences from the ions listed. Soak the electrode in distilled water for five minutes, then for five minutes in calcium standard solution to restore proper response.

**Table 3**  
Concentration of Possible Interferences causing a 10% Error at Various Levels of Calcium

Interferences (moles/liter)	$10^{-2}\text{M Ca}^{+2}$	$10^{-3}\text{M Ca}^{+2}$	$10^{-4}\text{M Ca}^{+2}$
$\text{Mg}^{+2}$	$1.0 \times 10^{+1}$	$1.0 \times 10^0$	$1.0 \times 10^{-1}$
$\text{Zn}^{+2}$	$1.0 \times 10^{+1}$	$1.0 \times 10^0$	$1.0 \times 10^{-1}$
$\text{Ba}^{+2}$	$7.0 \times 10^0$	$7.0 \times 10^{-1}$	$7.0 \times 10^{-2}$
$\text{K}^{+1}$	$4.0 \times 10^0$	$4.0 \times 10^{-1}$	$4.0 \times 10^{-2}$
$\text{Na}^{+1}$	$2.0 \times 10^0$	$2.0 \times 10^{-1}$	$2.0 \times 10^{-2}$
$\text{Ni}^{+2}$	$5.0 \times 10^{-1}$	$5.0 \times 10^{-2}$	$5.0 \times 10^{-3}$
$\text{Cu}^{+2}$	$4.0 \times 10^{-1}$	$4.0 \times 10^{-2}$	$4.0 \times 10^{-3}$
$\text{Fe}^{+2}$	$2.0 \times 10^{-2}$	$2.0 \times 10^{-3}$	$2.0 \times 10^{-4}$
$\text{Sr}^{+2}$	$6.0 \times 10^{-2}$	$6.0 \times 10^{-3}$	$6.0 \times 10^{-4}$
$\text{H}^{+1}$	$4.0 \times 10^{-2}$	$4.0 \times 10^{-3}$	$4.0 \times 10^{-4}$
$\text{Hg}^{+2}$	$4.0 \times 10^{-2}$	$4.0 \times 10^{-3}$	$4.0 \times 10^{-4}$
$\text{Pb}^{+2}$	$1.0 \times 10^{-4}$	$1.0 \times 10^{-5}$	$1.0 \times 10^{-6}$

## Interferences

(ppm)	1000 ppm CaCO <sub>3</sub>	100 ppm CaCO <sub>3</sub>	10 ppm CaCO <sub>3</sub>
Mg <sup>+2</sup>	2.43X10 <sup>5</sup>	2.43X10 <sup>4</sup>	2.43X10 <sup>3</sup>
Zn <sup>+2</sup>	6.53X10 <sup>5</sup>	6.53X10 <sup>4</sup>	6.53X10 <sup>3</sup>
Ba <sup>+2</sup>	9.60X10 <sup>5</sup>	9.60X10 <sup>4</sup>	9.60X10 <sup>3</sup>
K <sup>+1</sup>	1.56X10 <sup>5</sup>	1.56X10 <sup>4</sup>	1.56X10 <sup>3</sup>
Na <sup>+1</sup>	4.60X10 <sup>4</sup>	4.60X10 <sup>3</sup>	4.60X10 <sup>2</sup>
Ni <sup>+2</sup>	2.94X10 <sup>4</sup>	2.94X10 <sup>3</sup>	2.94x10 <sup>2</sup>
Cu <sup>+2</sup>	2.54X10 <sup>4</sup>	2.54X10 <sup>3</sup>	2.54X10 <sup>2</sup>
Fe <sup>+2</sup>	1.11X10 <sup>4</sup>	1.11X10 <sup>3</sup>	1.11X10 <sup>2</sup>
Sr <sup>+2</sup>	5.20X10 <sup>3</sup>	5.20X10 <sup>2</sup>	5.20X10 <sup>1</sup>
H <sup>+1</sup>	1.4 pH	2.4 pH	3.4 pH
Hg <sup>+2</sup>	8.0X10 <sup>2</sup>	8.0X10 <sup>2</sup>	8.0X10 <sup>1</sup>
Pb <sup>+2</sup>	2.0X10 <sup>1</sup>	2.0	2.0X10 <sup>-1</sup>

## Complexation

Sulfate, bicarbonate, and carbonate are the most common species that complex calcium ions. The level of calcium ions, the level of the complexing ion, the pH of the solution, and the total ionic strength of the solution determine the extent of the complexation. Complexation reduces the free calcium ion concentration and, since the electrode responds only to free calcium ions, a false reading results .

To avoid formation of CaSO<sub>4</sub>, the sulfate concentrations must be less than 5X10<sup>-4</sup>M (50 ppm). To avoid formation of CaCO<sub>3</sub> or formation of the CaHCO<sub>3</sub> complex, the pH of the solution should be less than 7, and the total carbonate/bicarbonate concentration should be less than 3X10<sup>-3</sup>M (280 ppm carbonate) .

## Temperature Influences

Samples and standards should be at the same temperature, since electrode potentials are influenced by changes in temperature. A 1°C difference in temperature results in a 4% error at the 1.0 X 10<sup>-3</sup> M level .

Provided that temperature equilibria has occurred, the calcium electrodes can be used at temperatures from 0°-40°C. Room temperature measurements are recommended, since measurements at temperatures quite different from room temperature may require equilibrium times up to one hour. Table 4 indicates the variation of the theoretical slope with temperature.

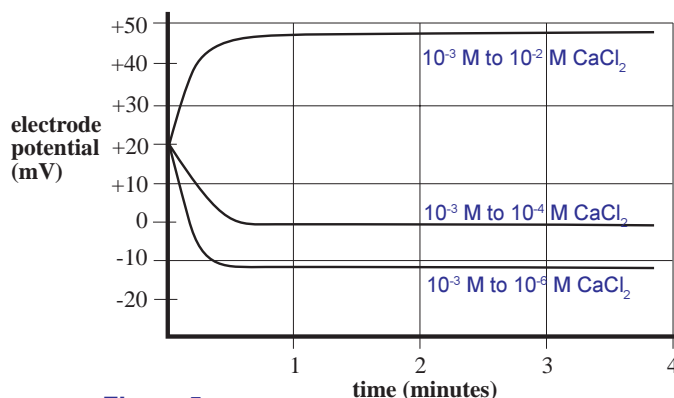
**TABLE 4: Temperature vs. Theoretical Values for the Electrode Slope**

Temp ( °C)	S
0	27.10
10	28.09
20	29.08
25	29.58
30	30.07
40	31.07

## Electrode Response

Plotting the electrode potential against the calcium concentration on semi-logarithmic paper results in a straight line with a slope of about 26 mV per decade. (Refer to Figure 3)

The time needed to reach 99% of the stable electrode potential reading, the electrode response time, varies from one minute or less for calcium concentration above  $1.0 \times 10^{-4} \text{ M}$  to several minutes near the detection limit. (Refer to Figure 5)



**Figure 5**  
Typical electrode time response to step changes in  $\text{CaCl}_2$

## Limits of Detection

The upper limit of detection in pure calcium chloride solutions is 1M. In the presence of other ions, the upper limit of detection is above  $1.0 \times 10^{-1} \text{ M}$ , but the possibility of a liquid junction potential developing at the reference electrode and the “salt extraction effect” are two limiting factors. Some salts may infuse into the electrode membrane at high salt concentrations causing deviation from theoretical response. Calibrate the electrode at four or five intermediate points, or dilute the sample, to measure samples between  $1.0 \times 10^{-1} \text{ M}$  and 1M.

The lower limit of detection is influenced by the slight water solubility of the ion exchanger used in the sensing portion of the electrode. Refer to Figure 1 for a comparison of the theoretical response to actual response at low levels of calcium chloride.

## pH Effects

The operating range of the calcium electrode is from pH 3 to pH 10. Use at other pH values can adversely affect the membrane. Hydrogen ion interferes with measurements of very low levels of calcium. Hydroxide ion will complex calcium ions.

## Electrode Life

The calcium electrode will last six months in normal laboratory use. On-line measurement might shorten operational lifetime to several months. In time, the response time will increase and the calibration slope will decrease to the point calibration is difficult and electrode replacement is required..

## Electrode Storage

The calcium electrodes may be stored for short periods of time in  $1.0 \times 10^{-2} \text{ M}$  calcium standard. For longer storage (longer than two weeks), rinse and dry the calcium membrane and cover the tip with any protective cap shipped with the electrodes. The reference portion of the combination electrode (or the outer chamber of the reference electrode) should be drained of filling solution, if refillable, and the rubber insert placed over the filling hole.

## Troubleshooting Guide

The goal of troubleshooting is the isolation of a problem through checking each of the system components in turn: the glassware, the electrodes, the standards and reagents, the sample, and the technique.

### Glassware/Plastic-ware

Clean glassware is essential for good measurement. Be sure to wash the glassware/plasticware well with a mild detergent and rinse very well with distilled or deionized water. Clean glassware will drain without leaving water droplets behind.

### Electrode

The electrodes may be checked by using the procedure found in the sections entitled *Electrode Slope Check*.

1. Be sure to use distilled or deionized water when following the procedures given in *Electrode Slope Check*.
2. If the electrode fails to respond as expected, see the sections *Measuring Hints* and *Electrode Response*. Repeat the slope check.
3. If the electrode still fails to respond as expected, substitute another calcium electrode that is known to be in good working order for the questionable electrode.
4. If the problem persists, the reagent may be of poor quality, interferences in the sample may be present or the technique may be faulty. (See *Standards & Reagents*, *Sample*, and *Technique* sections below.)
5. If another electrode is not available for test purposes, or if the electrode in use is suspect, review the instruction manual and be sure to:
  - Clean and rinse the electrodes thoroughly.
  - Prepare the electrodes properly.
  - Use the proper filling solution.
  - Adjust the pH and the ionic strength of the solution by the use of the proper ISA.
  - Measure correctly and accurately.
  - Review *Troubleshooting Hints*.

### Standards & Reagents

Whenever problems arise with the measuring procedure that has been used successfully in the past, be sure to check the standard and reagent solutions. If in doubt about the credibility of any of the reagents, prepare them again. Errors may result from contamination of the ISA, incorrect dilution of the standards, poor quality distilled/deionized water, or a simple mathematical miscalculation.

### Sample

Look for possible interferences, complexing agents, or substances which could affect the response or physically damage the sensing electrode if the electrodes work perfectly in the standard, but not in the sample.

Try to determine the composition of the samples prior to testing to eliminate a problem before it starts. (See *Measuring Hints*, *Sample Requirements*, and *Interferences*.)



## Technique

Be sure that the electrode's limit of detection has not been exceeded. Be sure that the analysis method is clearly understood and is compatible with the sample.

Refer to the instruction manual again, particularly the *General Preparation* and *Electrode Characteristics* sections.

If trouble still persists, call PASCO Technical Support.

## Troubleshooting Hints

Symptom	Possible Causes	Next Step
Out of Range Reading	defective electrode	check electrode operation
	electrodes not plugged in properly	unplug electrodes and reseal electrodes
	reference electrode not filled	be sure reference electrode is filled



# ***Technical Support***

## **Feedback**

If you have any comments about the product or manual, please let us know. If you have any suggestions on alternate experiments or find a problem in the manual, please tell us. PASCO appreciates any customer feedback. Your input helps us evaluate and improve our product.

## **To Reach PASCO**

For technical support, call us at 1-800-772-8700 (toll-free within the U.S.) or (916) 786-3800.

fax: (916) 786-3292

e-mail: [techsupp@pasco.com](mailto:techsupp@pasco.com)

web: [www.pasco.com](http://www.pasco.com)

## **Contacting Technical Support**

Before you call the PASCO Technical Support staff, it would be helpful to prepare the following information:

► If your problem is with the PASCO apparatus, note:

- Title and model number (usually listed on the label);
- Approximate age of apparatus;
- A detailed description of the problem/sequence of events (in case you can't call PASCO right away, you won't lose valuable data);
- If possible, have the apparatus within reach when calling to facilitate description of individual parts.

► If your problem relates to the instruction manual, note:

- Part number and revision (listed by month and year on the front cover);
- Have the manual at hand to discuss your questions.

